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On the origin of anisotropic lithiation in crystalline silicon over germanium: A first principles study

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ABSTRACT

Silicon (Si) and germanium (Ge) are both recognized as a promising anode material for high-energy lithium-ion batteries. Si is abundant and best known for its superior gravimetric energy storage capacity, while Ge exhibits faster charge/discharge rates and better capacity retention. Recently, it was discovered that Si lithiation exhibits strong orientation dependence while Ge lithiation proceeds isotropically, although they have the same crystalline structure. To better understand the underlying reasons behind these distinctive differences, we examine and compare the lithiation behaviors at the Li_4Si/*c*-Si(1 1 0) and Li_4Ge/*c*-Ge(1 1 0) model systems using ab initio molecular dynamics simulations. In comparison to lithiated *c*-Si, where a sharp amorphous–crystalline interface remains and advances rather slowly, lithiated *c*-Ge tends to loose its crystallinity rapidly, resulting in a graded lithiation front of fast propagation speed. Analysis of the elastic responses and dynamics of the host Si and Ge lattices clearly demonstrate that from the beginning of the lithiation process, Ge lattice responds with more significant weakening as compared to the rigid Si lattice. Moreover, the more flexible Ge lattice is found to undergo facile atomic rearrangements during lithiation, overshadowing the original crystallographic characteristic. These unique properties of Ge thereby contribute synergistically to the rapid and isotropic lithiation.

1. Introduction

Driven by the increasing demands for lithium-ion batteries (LIBs) with higher energy/power density, there has been a growing interest to replace the current graphite anode with alternative materials of higher Li storage capacities. Among them, silicon (Si) has received tremendous attention because it is abundant and has the highest known theoretical capacity (4200 mAh g^{-1} for $Li_{22}Si_5$ vs. 372 mAh g^{-1} for LiC_6) [1,2]. Germanium (Ge), second only to Si, has a high theoretical capacity of 1624 mAh g^{-1} ($Li_{22}Ge$ [3,4]), but has just begun to draw more research interests, especially in areas where it exhibits superior properties to Si. These include (i) higher intrinsic electrical conductivity [5], (ii) higher room-temperature Li diffusivity, enabling an ultrafast charging rate up to 1000 °C [6], and (iii) more resistive to surface oxidation than Si [7].

Being in the same column in the periodic table, Si and Ge both exist in the tetrahedrally bonded diamond structure with the lattice parameters differ only by 4%. Both are 'alloy-type' anodes, which form amorphous alloys with Li (*a*-Li_xSi/Li_xGe) upon room-temperature lithiation accompanied by large structural/volume changes, leading to early capacity fading [8–11]. Because of these similarities, one might expect Si and Ge to have very similar lithiation/delithiation behavior, but as highlighted by in situ characterizations, Si and Ge appear to have distinctively different responses to electrochemical lithiation/delithiation [12]. For instance, lithiation of crystalline Si (*c*-Si) exhibits a strong orientation-dependence (anisotropic), while crystalline Ge (*c*-Ge) is lithiated isotropically. Furthermore, in comparison to Si, Ge of comparable nano-architecture is able to withstand much faster charging rates with noticeably less crack formation. On the theoretical side, there have been many studies employing density functional theory (DFT) to examine Li incorporation in *c*-Si/*a*-Si bulks and nanowires [13–23] but a few on Ge [24,25]. Nonetheless, the fundamental understanding regarding the nature and origin of their dissimilar responses to lithiation is still limited.

In this paper, on the basis of DFT and ab initio molecular dynamics (AIMD) calculations, we first examine the structural evolution at the lithiation fronts in *c*-Si and *c*-Ge, and it turns out that the two systems are easily distinguished from one another in terms of lithiation mechanism and lithiation propagation speed. To explain the origin of these differences, we investigate the elastic responses

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of Si and Ge lattices upon lithiation as well as the role of their lattice dynamics. The fundamental findings may assist the rational design of the next-generation high performance Si- and Ge-based anodes.

2. Computational methods

Quantum mechanical calculations reported herein were performed on the basis of density functional theory (DFT) within the generalized gradient approximation (GGA-PW91) [26], as implemented in the Vienna Ab-initio Simulation Package (VASP) [27–29]. The projected augmented wave (PAW) method with a plane-wave basis set was used to describe the interaction between core and valence electrons. An energy cutoff of 350 eV was used for geometric optimization of model structures for the a-Li_4Si/Si(1 1 0) and a-Li_4Ge/Ge(1 1 0) interfaces; all atoms were fully relaxed using the conjugate gradient method till residual forces are smaller than 5×10^{-2} eV Å^{-1}. For Brillouin zone sampling, a $(2 \times 2 \times 2)$ k-point mesh was used in the scheme of Monkhorst-Pack [30]; the k-point mesh size should be sufficient considering the disordered nature of the interface systems.

The initial structure for the a-Li_4Si/Si(1 1 0) interface was prepared by stacking an a-Li_4Si bulk model on top of a c-Si supercell in the [1 1 0] direction. The a-Li_4Si model structure consisted of 51 Li and 13 Si atoms has dimensions of 10.914 Å × 11.5761 Å × 8.5576 Å, which were tailored to match the same dimensions of the c-Si lattice in the x and y directions [see Ref. [15] for detailed computational methods]. We used the GGA-optimized lattice constant of 5.457 Å for c-Si, and the 96-atom c-Si supercell has dimensions of 10.914 Å × 11.5761 Å × 15.5761 Å. The a-Li_4Si/Si(1 1 0) system was fully relaxed and then annealed at 500 K for 1 ps to allow sufficient atomic rearrangement, followed by geometry optimization. The a-Li_4Ge/Ge(1 1 0) interface was generated following exactly the same procedures; the a-Li_4Ge model structure consisted of 51 Li and 13 Ge atoms has dimensions of 12.2529 Å × 11.5532 Å × 7.4895 Å, the GGA-optimized Ge lattice constant is 5.777 Å, and the 96-atom c-Ge supercell has dimensions of 12.2529 Å × 11.5532 Å × 23.3557 Å. To simulate the lithiation processes, ab initio molecular dynamics (AIMD) simulations were performed at 1000 K; a time step of 1 fs was used while the temperature was controlled via Nose–Hover thermostat.

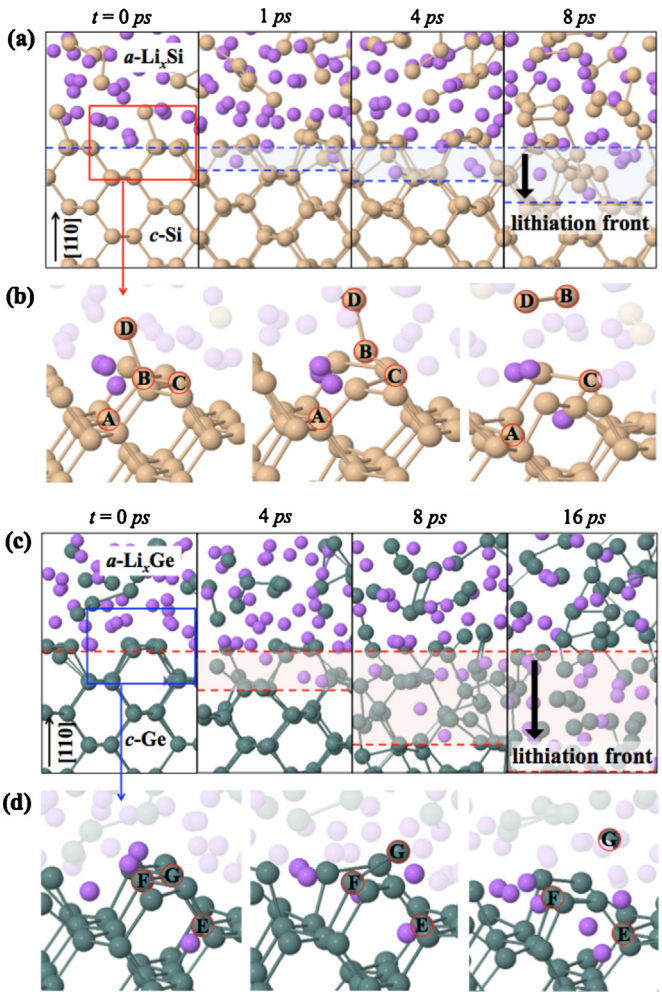

Fig. 1. (a) Structural evolution of the a-Li_4Si/Si(1 1 0) interface with annealing time t = 0, 1, 4 and 8 ps, corresponding to different stages of lithiation. (b) A close up view of interfacial Si atoms break off as dimers (Si_B—Si_D). (c) Structural evolution of the a-Li_4Ge/Ge(1 1 0) interface with annealing time t = 0, 4, 8 and 16 ps. (d) Interfacial Ge atoms mostly break off as monomers (Ge_G).

3. Results and discussion

To examine the anisotropic lithiation behavior of c-Si, the a-Li_4Si/Si(1 1 0) interface was constructed and annealed via AIMD; an annealing temperature of 1000 K was chosen such that the thermal energy is sufficient to agitate atomic movements but far below the melting point of c-Si. The abrupt a-Li_4Si/Si(1 1 0) system can be a realistic representation of the lithiation front considering the following kinetic and energetic points of view. It is now well known that upon lithiation, an a-Li_xSi layer is formed spontaneously at the surface because Li atoms diffuse preferentially along the surface, and driven by the concentration gradient and energetically favorable Li–Si mixing, Li atoms are incorporated into the Si matrix, forming Li_xSi alloys [14,18,19,31]. With the rising Li concentration (x), Li diffusivity (D_{Li}) tends to increase by orders of magnitude [14,15,32], suggesting the solid-state amorphization (converting c-Si into a-Li_xSi alloys) is kinetically feasible at room temperature and such process continues till the most stable alloy composition is reached around x = 4 [15,31]. Given this picture, lithiation of c-Si will be controlled by the reaction at the a-Li_4Si/c-Si interface. Here, only the (1 1 0) crystal orientation is considered since it has been found to be the most favorable facet for Si lithiation [17,25].

Fig. 1(a) shows the structural evolution of the a-Li_4Si/Si(1 1 0) interface with annealing time (t = 0, 4, 8 and 16 ps). During the simulation, the amorphous–crystalline interface (ACI) remains sharp, while Li atoms diffuse into the c-Si region very slowly despite the high annealing temperature. This clearly demonstrates that the lithiation process proceeds in a layer-by-layer fashion, leading to the anisotropic lithiation of c-Si, which is consistent with previous experimental and theoretical findings [17,23]. As Li atoms diffuse into the c-Si region, as shown in Fig. 1(b), the interfacial Si atoms dissolve into the a-Li_4Si region preferentially as dimers (like Si_B—Si_D), apparently due to the weakening of their back bonds (like Si_A—Si_B and Si_B—Si_C) as a result of charge transfer from Li atoms [13,15,17]. In addition, only the interface Si layer is highly distorted whereas the crystallinity in the subinterface layers remains nearly intact, resulting in the sharp ACI.

Next, we examined the lithiation behavior of c-Ge; for direct comparison, the a-Li_4Ge/Ge(1 1 0) interface was constructed and annealed at the same temperature (1000 K). As shown in Fig. 1(c), there appears to be distinct differences between the Ge and Si cases. Compared to the Si case, Li diffusion into the c-Ge region is much faster while the Ge lattice distortion is farther extended beyond the interface layer, resulting in the graded/disordered lithiation front. This suggests that the lithiation of c-Ge may occur isotropically, in contrast to the anisotropically lithiated c-Si, consistent with previous experimental observations [12]. In addition, as Li atoms diffuse into the c-Ge region [Fig. 1(d)], the interfacial Ge atoms break off

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